

TREATING SOLUTION FOR SURFACE TREATMENT OF METAL  
AND A METHOD FOR SURFACE TREATMENT

### Technical Field

The present invention relates to a treating solution for the surface treatment of a metal which may deposit a surface-treated film having excellent corrosion resistance after being coated on the surface of a metal material of a structural construction such as a car body consisting of a single material or two to four materials selected from the group consisting of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material independently or simultaneously.

### Background Art

As the method of forming on a metal surface a surface-treated film having excellent corrosion resistance after being coated, a zinc phosphate treatment and a chromate treatment are currently used as ordinary methods. According to the zinc phosphate treatment, it is possible to deposit a film having excellent corrosion resistance on the surface of a steel such as cold-rolled steel plate, zinc-plated steel plate and some of aluminum alloys. However, in the zinc phosphate treatment, the generation of sludge, which is the byproduct of the reaction cannot be avoided, and depending on the kind of aluminum alloy, sufficient corrosion resistance after being coated cannot be obtained. While, in the case of an aluminum alloy, it is possible to obtain sufficient properties after being coated by applying the chromate treatment. Concerning the recent environmental regulations, the chromate treatment which contains harmful hexavalent chrome in the treating solution is more likely to be avoided. As the method for metal surface treatment, which does not contain a harmful component in the treating solution, various methods have been proposed as described below.

For example, in JP 2000-204485 A, a compound containing a nitrogen atom having a lone electron-pair and a non-chrome coating agent for metal surface treatment containing said compound and a zirconium compound are suggested. This method may obtain a surface-treated film which is excellent in corrosion resistance and adhesiveness after being coated, and yet does not contain harmful hexavalent chrome by coating the above-mentioned coating agent. However, in the case of the method, the metal material which can be treated is limited to aluminum alloys only, and, it is difficult to be applied to a structural construction having a complex structure such as a car body, because the surface-treated film is formed by coating and drying.

Further, as the method of depositing a metal surface-treated film having excellent adhesiveness and corrosion resistance after being coated due to the chemical reaction, various methods such as those disclosed in JP 56-136978 A, JP 8-176841 A, JP 9-25436 A and JP 9-31404 A have been suggested. However, in any of these methods, the metal material which can be treated is limited to the aluminum alloy only, originally having excellent corrosion resistance; these methods may not deposit a surface-treated film on the surface of ferriferrous material or zinciferous material.

Furthermore, proposed is a method of forming a metal surface-treated film having excellent corrosion resistance and adhesion after being coated, by using a surface-treating agent composed of metal acetylacetonate and water-soluble inorganic titanium compound or water-soluble inorganic zirconium compound (see JP 2000-199077). By this method, metal materials to be treated may include magnesium, magnesium alloys, zinc and zinc-plated alloys other than aluminum alloys. However, by this method, it is difficult to form a surface-treated film on a surface of a ferriferrous material such as cold-rolled steel, and is not possible to treat a ferriferrous material at the same time.

Still further, a method for metal surface treatment by a chrome-free coating acid composition by coating an aqueous solution containing a component which can form a film having excellent corrosion resistance over the surface of metal, then baking and drying without rinsing with water so that the film is fixed (see JP 5-195244 A). This method does not involve any chemical reaction to form a film, so this method may form a film on the surface of a metal such as zinc-plated steel plate, cold-rolled steel plate or an aluminum alloy. However, similarly to the invention disclosed in the above-mentioned JP 2000-204485 A, since the film is formed by coating and drying, it is difficult to form a uniform film on the surface of a structural construction having a complex structure such as a car body.

As mentioned above, according to the prior arts, it was impossible to perform a surface treatment providing excellent corrosion resistance and adhesion on a car body and the like composed of two to four metal materials of a ferriferous material such as cold-rolled steel plate, a zinciferous material such as zinc-plated steel plate, an aluminiferous material and a magnesiferous material simultaneously with a treating solution containing no harmful component to the environment and not generating waste sludge.

#### Disclosure of the Invention

The object of the present invention is to provide a treating solution for surface treatment of a metal which forms a surface-treated film having excellent corrosion resistance after being coated on the surface of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material, which does not contain a harmful component to the environment and does not generate sludge to be wasted, which was not accomplished by the prior arts. Further, the object of the present invention is to provide a treating solution for metal surface treatment to form a surface-treated film of a uniform component having excellent

corrosion resistance after being coated on the surface of a metal material composing a structural construction such as a car body consisting of two to four materials selected from the group consisting of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material by the same component simultaneously under a uniform condition. Another object of the present invention is to provide a method for treatment using the treating solution.

The inventors of the present invention have conducted intensive study to solve the above-mentioned problems and have accomplished a treating solution for surface treatment of a metal and a method for surface treatment which were not provided by the prior art.

That is, the present invention is a treating solution for the surface treatment of a metal, which is an aqueous surface treating solution for treating independently each metal material or simultaneously two or more metal materials selected from the group consisting of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material, the treating solution containing 5 to 5000 ppm of at least one compound selected from the group consisting of a zirconium compound and a titanium compound, calculated as the metal element, and 0.1 to 100 ppm of free fluorine ion, and having pH 2 to 6.

The treating solution for the surface treatment of a metal may further contain at least one compound selected from the group consisting of a calcium compound, a magnesium compound and a strontium compound, wherein the concentration of the compound calculated as a metal element is 5 to 100 ppm in the case of the calcium compound, 10 to 5000 ppm in the case of the magnesium compound and 10 to 5000 ppm in the case of the strontium compound. It is desirable that the treating solution for the surface treatment of a metal further contains 1000 to 50000 ppm of a nitrate group. It is desirable that the treating solution for the surface treatment of a metal further contains at least one oxygen acid and/or salt of an oxygen

acid selected from the group consisting of  $\text{HClO}_3$ ,  $\text{HBrO}_3$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{HMnO}_4$ ,  $\text{HVO}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{WO}_4$ ,  $\text{H}_2\text{MoO}_4$ . The treating solution for the surface treatment of a metal may further contain at least one polymer compound selected from the group consisting of water-soluble polymer compounds and water-dispersible polymer compounds, and may further contain at least one surface-active agent selected from the group consisting of nonionic surface-active agents, anionic surface-active agents and cationic surface-active agents.

The present invention is also a method for the surface treatment of a metal comprising contacting, independently, each metal material or, simultaneously, two or more metal materials selected from the group consisting of ferriferous materials, zinciferous materials, aluminiferous materials and magnesiferous materials with a treating solution for surface treatment. In the method for surface treatment, after being contacted with the treating solution for surface treatment, it is possible to further contact the metal material or the two or more metal materials with an acidic aqueous solution of a compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium, with or without washing by water, or it is possible to further contact the metal material or the two or more metal materials with a treating solution containing at least one polymer compound selected from water-soluble polymer compounds and water-dispersible polymer compounds.

Moreover, the present invention is the method for the surface treatment of a metal comprising, electrolytic treating in the treating solution for surface treatment, wherein, independently, each metal material or simultaneously two or more metal materials selected from the group consisting of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material are a cathode. In the method for surface treatment, after electrolytic treating in the treating solution for surface treatment, it is possible to further contact the metal material or the two or more metal

materials with an acidic aqueous solution of a compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium, with or without washing by water, or it is possible to further contact the metal material or the two or more metal materials with a treating solution containing at least one polymer compound selected from water-soluble polymer compounds and water-dispersible polymer compounds, with or without washing by water.

The present invention is a method for the surface treatment of a metal comprising contacting, independently, each metal material or, simultaneously, two or more metal materials selected from the group consisting of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material, whose surfaces are not degreased and cleaned, with the treating solution for surface treatment containing at least one surface-active agent selected from the group consisting of the above-described nonionic surface-active agents, anionic surface-active agents and cationic surface-active agents.

Furthermore, the present invention is a metal material having a surface-treated film containing at least one metal element selected from the group consisting of titanium and zirconium formed on a surface of an iron metal material by the method for surface treatment, wherein an adhesion amount of the surface-treated film, calculated as the metal element, is 30 mg/m<sup>2</sup> or more; in the case when it is formed on a surface of zinc metal material, the adhesion amount of the surface-treated film, calculated as the metal element, is 20mg/m<sup>2</sup> or more; in the case when it is formed on a surface of an aluminum metal material, the adhesion amount of the surface-treated film, calculated as the metal element, is 10mg/m<sup>2</sup> or more; and in the case when it is formed on the surface of a magnesium metal material, the adhesion amount of the surface-treated film, calculated as the metal element, is 10mg/m<sup>2</sup> or more.

### Brief Description of Drawings

Fig.1 is a plane view of the test plate used in the Examples and Comparative Examples.

Fig.2 is an elevation view of the test plate.

### Best Mode for Carrying out the Invention

The present invention relates to the art characterized in depositing a surface-treated film having excellent corrosion resistance after being coated, by surface treatment on, independently, each metal material or, simultaneously, two or more metal materials selected from the group consisting of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material. In the present invention, a ferriferous material is an iron metal such as a cold-rolled steel plate, a hot-rolled steel plate, cast iron or sintered steel. A zinciferous material is a die-casting zinc or a zinc-containing plating. This zinc-containing plating means a metal plating with zinc or a zinc alloy composed of zinc and other metals (for example, at least one metal selected from the group consisting of nickel, iron, aluminum, manganese, chromium, magnesium, cobalt, lead and antimony) and inevitable impurities, and the methods for such plating include hot galvanizing, electric plating and vapor-deposition plating, and are not limited to these methods. Further, the aluminiferous material is an aluminum alloy board such as a JIS 5000 series aluminum alloy or JIS 6000 series aluminum alloy, or an aluminum alloy die cast represented by ADC-12. Still more, the magnesiferous material is a metal board or a die cast made of a magnesium alloy.

The present invention can be applied to a structural construction which contains one metal material mentioned above alone in the composing parts or to a structural construction which contains two to four metal materials mentioned above in the composing parts. In the case of applying the present invention to the structural construction which contains two to

four metal materials mentioned above, it is possible to treat the surfaces of two to four metal materials at the same time. In the case of treating the surfaces of two to four metal materials at the same time, the different metals can be in the condition not contacting each other or in the condition being joined and contacting by means of a joining method such as welding, adhesion or riveting.

The treating solution for the surface treatment of a metal of the present invention contains 5 to 5000 ppm of at least one compound selected from the group consisting of a zirconium compound and a titanium compound, calculated as the metal element, and 0.1 to 100 ppm of free fluoride ion, and further has a pH of 2 to 6. Here, as the zirconium compound used in the present invention,  $ZrCl_4$ ,  $ZrOCl_2$ ,  $Zr(SO_4)_2$ ,  $ZrOSO_4$ ,  $Zr(NO_3)_4$ ,  $ZrO(NO_3)_2$ ,  $H_2ZrF_6$ , a salt of  $H_2ZrF_6$ ,  $ZrO_2$ ,  $ZrOBr_2$  and  $ZrF_4$  can be mentioned. As the titanium compound,  $TiCl_4$ ,  $Ti(SO_4)_2$ ,  $TiOSO_4$ ,  $Ti(NO_3)_4$ ,  $TiO(NO_3)_2$ ,  $TiO_2OC_2O_4$ ,  $H_2TiF_6$ , a salt of  $H_2TiF_6$ ,  $TiO_2$  and  $TiF_4$  can be mentioned. In the present invention, a zirconium compound is desirably used.

The desirable concentration of at least one compound selected from the group consisting of a zirconium compound and a titanium compound is 5 to 5000 ppm, calculated as the metal element (that is, as zirconium and/or titanium), and the more desirable concentration is 10 to 3000 ppm. The film obtained by using the treating solution for the surface treatment of a metal and the method for surface treatment of the present invention is an oxide or hydroxide of zirconium or titanium. Therefore, when the concentration of the compound selected from the group consisting of a zirconium compound and a titanium compound, calculated as zirconium and/or titanium, is smaller than 5 ppm, it is difficult to obtain a sufficient adhesion amount to attain corrosion resistance in a practical period of time for treating, because the concentration of the main component of the film is too low. On the contrary, when the concentration is larger than 5000 ppm, a sufficient adhesion amount can be obtained, but it is not effective to



improve the corrosion resistance and is disadvantageous from the economical view point.

The zirconium compound and the titanium compound can be easily dissolved in the acidic solution, but are not stable in the alkaline solution, and easily deposit as an oxide or hydroxide of zirconium or titanium. The desirable pH of the treating solution for the surface treatment of a metal of the present invention is a pH of 2 to 6, more desirably, a pH of 3 to 6. When the metal material to be treated is in contact with the treating solution for the surface treatment of a metal of the present invention in the desirable pH range, the dissolving reaction of the metal material to be treated occurs. By the dissolving of the metal material to be treated, the pH becomes higher at the surface of the metal material to be treated, and the oxide or hydroxide of zirconium or titanium deposits as a film on the surface of the metal material to be treated.

The treating solution for the surface treatment of a metal of the present invention has free fluorine ions existing therein. To allow free fluorine ions to exist, the fluorine compound is added into the treating solution for the surface treatment of a metal. As the supplying source of the free fluorine ion, hydrofluoric acid,  $\text{H}_2\text{ZrF}_6$  and salts of  $\text{H}_2\text{ZrF}_6$ ,  $\text{H}_2\text{TiF}_6$ , salts of  $\text{H}_2\text{TiF}_6$ ,  $\text{H}_2\text{SiF}_6$ , salts of  $\text{H}_2\text{SiF}_6$ ,  $\text{HBF}_4$  and salt of  $\text{HBF}_4$ ,  $\text{NaHF}_2$ ,  $\text{KHF}_2$ ,  $\text{NH}_4\text{HF}_2$ ,  $\text{NaF}$ ,  $\text{KF}$  and  $\text{NH}_4\text{F}$  can be mentioned. The free fluorine ion has an effect of improving the stability of the zirconium compound and titanium compound in the treating solution for the surface treatment of a metal. Further, the free fluorine ion has a function of promoting the dissolving reaction of any of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material, which are the metal materials to be surface-treated in the present invention. Therefore, by allowing free fluorine ions to exist therein by adding a fluorine compound, the stability of the treating solution for the surface treatment of a metal of the present invention is

improved, and further the reactivity to the metal material to be treated can be improved.

The inventors of the present invention have previously suggested a composition for surface treatment and a treating solution for surface treatment of a metal containing at least one of iron and zinc in WO02/103080 as follows. That is, the composition for surface treatment and treating solution for surface treatment of a metal use a titanium compound or a zirconium compound and a fluorine-containing compound, wherein the ratio A/B is set within the specific range from 0.06 to 0.18, where A refers to the total mole weight of metal elements in the composition for surface treatment and the treating solution for surface treatment of a metal and B refers to the mole weight when the total fluorine atoms in the fluorine-containing compound is calculated as HF. According to the present invention, it is possible to perform surface treatment on, independently, one metal material or, simultaneously, two or more metal materials selected from the group consisting of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material, even if out of the above-mentioned specific range of the ratio, by regulating the concentration of the metal element in the titanium compound and zirconium compound, pH and the concentration of free fluorine ion.

It was impossible in the prior arts to perform the surface treatment on two or more metal materials mentioned above at the same time, because the respective reactivity of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material are different. In the present invention, it is possible to perform the surface treatment independently on each metal material or simultaneously on each metal material or two or more metal materials selected from the group consisting of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material, because the stability of the treating solution for the surface treatment of a metal and the

reactivity can be balanced arbitrarily by regulating the concentration of free fluorine ions.

In the present invention, the concentration of free fluorine ion means the concentration of fluorine ion measured by an ion electrode which is on the market. The concentration of free fluorine ion in the treating solution for surface treatment of metal of the present invention is desirably 0.1 to 100 ppm, and more desirably 2 to 70 ppm. In the case where the concentration of free fluorine ion is higher than 100 ppm, the dissolving reaction of the metal material to be treated is promoted. However, since the zirconium compound and the titanium compound in the treating solution for the surface treatment of a metal are very stable, even if the pH of the surface of the metal material to be treated increases, it becomes difficult to deposit as a film. In the case where the concentration of free fluorine ion is lower than 0.1 ppm, the effect for the improvement of the stability of the treating solution for the surface treatment of a metal and the reactivity thereof is small, and thus, it is no longer advantageous for the treating solution to contain free fluorine ion.

Other than the effect for the improvement of the stability and reactivation of the treating solution for the surface treatment of a metal, the free fluorine ion of the present invention has a role of keeping the eluted component, by dissolution of the metal material to be treated, stable in the treating solution for the surface treatment of a metal. In the case of a zinc phosphate treatment of the prior arts, sludges generated, because, for example, iron ions eluted from an iron metal material reacts with phosphoric acid and forms iron phosphate which is an insoluble salt. The treating solution for the surface treatment of a metal of the present invention may also contain a phosphoric acid group, but, if the concentration of the phosphoric acid group is in excess of 1.0g/L, sludge can be generated. In the case where the treating amount of the metal material to be treated is

remarkably large with respect to the volume of the bath for treatment, one or more compounds selected from the group, for example, consisting of an inorganic acid such as a sulfuric acid or hydrochloric acid; an organic acid such as acetic acid, oxalic acid, tartaric acid, citric acid, succinic acid, gluconic acid or phthalic acid; and a chelating agent which can chelate an eluted component, may be added in the treating solution to thereby solubilize the eluted component.

The treating solution for the surface treatment of a metal in the present invention may contain at least one compound selected from the group consisting of a calcium compound, a magnesium compound and a strontium compound. The present invention performs surface treatment on each metal material independently or two to four materials simultaneously selected from the group consisting of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material by regulating the concentration of free fluorine ion in the aqueous solution containing a zirconium compound and a titanium compound of specific concentration within the specified range. Here, the metal elements (calcium, magnesium or strontium) contained in the above-mentioned calcium compound, magnesium compound or strontium compound have a function of maintaining the concentration of free fluorine ion in an aqueous solution to a certain value by generating a salt of fluorine and a fluorinated compound in the aqueous solution. Due to the function, when the surface of various kinds of metal materials are treated at the same time, the optimum deposit amount of the film can be obtained on each metal material to be treated because a certain concentration of free fluorine ion can be maintained, regardless of the ratio among the materials used.

As examples of calcium compounds, magnesium compounds or strontium compounds which can be used in the present invention, for example, oxides, hydroxides, chlorides, sulfates, nitrates and carbonates of these metal elements can be mentioned. Further, besides calcium compounds, magnesium compounds and

strontium compounds, the compound which has a function of maintaining the concentration of free fluorine ion constant can be used regardless of whether an organic compound or an inorganic compound is used.

The concentration of the magnesium compound or the strontium compound which can be used in the present invention is desirably 10 to 5000 ppm as the metal element, and more desirably is 100 to 3000 ppm. In the case of the calcium compound, the desirable concentration as calcium is 5 to 100 ppm and a more desirable concentration is 5 to 50 ppm, because the solubility of calcium is remarkably small. When the concentration of these compounds is higher than the upper limit, the stability of the treating solution for the surface treatment of a metal may decrease, and the continuous treatment is interrupted. When the concentration of these compounds is lower than the lower limit, the deposit amount of the film, particularly on a ferriferous material, decreases.

In the treating solution for the surface treatment of a metal of the present invention, desirably 1000 to 50000 ppm, more desirably 1000 to 30000 ppm, of a nitric acid group may be added. The nitric acid group acts as an oxidizing agent and has a function of promoting a film depositing reaction of the present invention and a function of improving the solubility of the above-mentioned calcium compound, magnesium compound or strontium compound in the treating solution for the surface treatment of a metal. Therefore, even if the concentration of the nitric acid group is lower than 1000 ppm, a film having an excellent corrosion resistance can be deposited. However, in the case where the concentration of the above-mentioned calcium compound, magnesium compound or strontium compound is high, the stability of the treating solution for the surface treatment of a metal may decrease. A concentration of the nitric acid group of 50000 ppm is sufficient and it is disadvantageous to add more nitric acid group from the economical view point.

Further, in the treating solution for the surface treatment of a metal of the present invention, at least one oxygen acid and/or salt of an oxygen acid selected from the group consisting of  $\text{HClO}_3$ ,  $\text{HBrO}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{HMnO}_4$ ,  $\text{HVO}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{WO}_4$  and  $\text{H}_2\text{MoO}_4$ . The oxygen acid or salt thereof acts as an oxidizing agent for the materials to be treated and promotes the film-forming reaction in the present invention. The concentration of these oxygen acids or salts thereof to be added is not restricted, but adding an amount from 10 to 5000 ppm exhibits sufficient effect as the oxidizing agent.

Still further, in the treating solution for the surface treatment of a metal of the present invention, at least one polymer compound selected from the group consisting of water-soluble polymer compounds and water-dispersible polymer compounds may be added. The metal element whose surface is treated by using the treating solution for the surface treatment of a metal of the present invention has enough corrosion resistance, but, if an additional function such as lubricity is required, it is possible to improve the physical property of the film by adding a preferably selected polymer according to the desired function. As the examples of the above-mentioned water-soluble polymer compounds and water-dispersible polymer compounds, polymer compounds which are generally used for the surface treatment of a metal such as a polyvinyl alcohol, a poly(metha)acrylic acid, a copolymer of acrylic acid and methacrylic acid, a copolymer of ethylene with an acrylic monomer such as (metha)acrylic acid or (metha)acrylate, a copolymer of ethylene and vinyl acetate, a polyurethane, an amino-modified phenol resin, a polyester resin and an epoxy resin can be used.

The method for surface treatment of the present invention can be illustrated as follows. Namely, the surface is merely treated by a degreasing treatment according to an ordinary method and the cleaned metal material to be treated is brought into contact with the treating solution for the surface treatment of a metal. Accordingly, a film composed of an oxide

and/or hydroxide of a metal element selected from the group consisting of zirconium and titanium is deposited and a surface-treated film layer having a good adhesiveness and corrosion resistance is formed. As the substantial method for this contacting process, any kind of treatment, e.g., spraying treatment, immersion treatment or pouring treatment can be used, and the properties of the product will not be influenced by the treating method. From the chemical view point, it is difficult to obtain the hydroxide of the above-mentioned metal as a pure hydroxide and, in general, the oxide of the above-mentioned metal to which hydrated water is attached is considered as a hydroxide. Therefore, the hydroxide of the metal finally becomes the oxide by heating. The structure of the surface-treated layer of the present invention is considered to be a state where the oxide and hydroxide are mixed when dried at an ordinary temperature or at a low temperature after surface treatment. When dried at a high temperature after the surface treatment, the structure of the surface-treated layer is considered to be a state of an oxide alone or oxide rich.

In the present invention, the condition of using the treating solution for the surface treatment of a metal is not restricted. The reactivity of the treating solution for the surface treatment of a metal of the present invention can be voluntarily regulated by changing the concentration of the zirconium compound or titanium compound and the concentration of free fluorine ion in the treating solution for the surface treatment of a metal. Therefore, the treating temperature and treating period of time can be changed voluntarily in combination with the reactivity of the treating bath.

Further, to the treating solution for the surface treatment of a metal, at least one surface-active agent selected from the group consisting of a nonionic surface-active agent, an anionic surface active agent and a cationic surface active agent can be added. In the case where the surface of a metal material is treated with this treating

solution for the surface treatment of a metal, a good film can be formed without a previous degreasing and cleaning treatment being performed on the metal material to be treated. That is, this treating solution for the surface treatment of a metal can be used also as a surface-treating agent and a degreasing agent.

Furthermore, for the treatment of the surface of a metal using the treating solution for the surface treatment of a metal of the present invention, the method of carrying out electrolysis in the treating solution for the surface treatment of metal is to have a metal material to be treated act as a cathode. When the electrolysis treatment is carried out using the metal material to be treated as a cathode, a reduction occurs at the surface of the cathode and the pH goes up. Along with the elevation of the pH, the stability of the zirconium compound and/or titanium compound at the surface of the cathode deteriorates, and the surface-treated film is deposited as an oxide or a hydroxide containing water.

Still further, the effect of the present invention can be improved when, after being contacted with the treating solution for the surface treatment of a metal, or after being electrolyzed in the treating solution for the surface treatment of a metal with or without being washed by water, the metal material is brought into contact with the acidic solution of the compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium, or with a treating solution containing at least one polymer compound selected from the group consisting of a water-soluble polymer compound and water-dispersible polymer.

The surface-treated film layer obtained by the present invention is characterized as a thin film and exhibits an excellent coating property but, depending on the surface condition of the metal material to be treated, sometimes tiny defects may be formed in the surface-treated film layer. By bringing the layer in contact with the acidic solution of the



compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium or the treating solution containing at least one polymer compound selected from the group consisting of a water-soluble polymer compound and a water-dispersible polymer, the tiny defects are covered and the corrosion resistance can be further improved.

The compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium is not restricted and it is possible to use oxides, hydroxides, fluorides, complex fluorides, chlorides, nitrates, oxynitrates, sulfates, oxysulfates, carbonates, oxycarbonates, phosphates, oxyphosphates, oxalates, oxyoxalates, and organic metal compounds and the like. Further, desirably, the pH of the acidic solution containing the metal element is 2 to 6 and can be adjusted with an acid such as phosphoric acid, nitric acid, sulfuric acid, hydrofluoric acid, hydrochloric acid and an organic acid or alkali such as sodium hydroxide, potassium hydroxide, lithium hydroxide, salts of an alkali metal, an ammonium salt or amines.

Further, as at least one polymer compound selected from the above-mentioned water-soluble polymer compound or water-dispersible polymer compound, for example, a polyvinyl alcohol, a poly(metha)acrylic acid, a copolymer of acrylic acid and methacrylic acid, a copolymer of ethylene with an acrylic monomer such as (metha)acrylic acid or (metha)acrylate, a copolymer of ethylene and vinyl acetate, a polyurethane, an amino-modified phenol resin, a polyester resin or an epoxy resin, tannin and tannic acid and salts thereof, and phytic acid can be used.

The present invention may remarkably improve the corrosion resistance of a metal material by providing a surface-treated film layer composed of an oxide and/or hydroxide of a metal element selected from zirconium and/or titanium on the surface of a metal material to be treated. The oxide and hydroxide of the above-mentioned metal elements have

a physical property characterized by being not damaged by an acid or alkali and chemically stabilized. In the actual corrosive environment for the metal, at the anode where the metal elution phenomenon occurs, the pH becomes lower, while, at the cathode where reduction occurs, the pH becomes higher. Therefore, the surface-treated film of less resistance to an acid and an alkali may dissolve under the corrosive environment and its effect would be lost. Since the main component of the surface treated film layer of the present invention is resistive to acid or alkali, the excellent effect can be maintained under the corrosive environment.

Since the oxide and hydroxide of the above-mentioned metal elements form a network structure mediated by a metal and an oxide, it becomes a very good barrier film. The corrosion of the metal material, which can vary depending on the environment of use, generally, is an oxygen-demanding type of corrosion in an atmosphere in which water and oxygen exist, and the speed of the corrosion is promoted by the presence of components such as chlorides. Having a barrier effect against water, an acid and a corrosion-promoting component, the surface-treated film layer of the present invention may exhibit excellent corrosion resistance.

For the purpose of enhancing the corrosion resistance of an iron metal material such as cold-rolled steel plate, hot-rolled steel plate, cast iron and sintered steel using the above-mentioned barrier effect, the adhesion amount over 30 mg/m<sup>2</sup>, calculated as the metal element, is desirably over 40 mg/m<sup>2</sup> and, more desirably, over 50 mg/m<sup>2</sup>. For the purpose of enhancing the corrosion resistance of a zinc metal material such as zinc, zinc-plated steel plate and alloyed hot-dip zinc-coated steel plate, an adhesion amount over 20 mg/m<sup>2</sup>, calculated as the metal element, is necessary, desirably over 30 mg/m<sup>2</sup>. Further, for the purpose of enhancing the corrosion resistance of an aluminiferous materials such as cast aluminum and an aluminum alloy plate, an adhesion amount over 10 mg/m<sup>2</sup>, calculated as the metal element, is necessary, desirably over

20 mg/m<sup>2</sup>. For the purpose of enhancing the corrosion resistance of magnesiferous materials such as a magnesium alloy plate and cast magnesium, an adhesion amount over 10 mg/m<sup>2</sup>, calculated as the metal element, is necessary, desirably over 20 mg/m<sup>2</sup>. Referring to the adhesion amount, there is no upper limit. However, when the amount exceeds 1g/m<sup>2</sup>, cracks are easily generated on the surface-treated film layer and it becomes difficult to form a uniform film. Therefore, in any case of an iron metal material and zinc metal material and aluminiferous material, the desirable upper limit of the adhesion amount is 1 g/m<sup>2</sup>, more desirably 800 mg/m<sup>2</sup>.

#### Examples

The effects of the treating solution for the surface treatment of a metal and the method for surface treatment of the present invention will be illustrated specifically in accordance with the Examples and Comparative Examples below. A material to be treated, a degreasing agent and a coating used therein are arbitrarily selected from materials which are on the market and are not intended to restrict the actual uses of the treating solution for the surface treatment of a metal and the method for surface treatment of the present invention.

#### Test plate

As the test plates, cold-rolled steel plates, hot-dip zinc-coated steel plates, aluminum alloy plates and magnesium alloy plates are used in the Examples and Comparative Examples. The abbreviations and specifications of these test plates are shown below. For the evaluation of the appearance after surface treatment, the test plate prepared by joining three metal materials of SPC, GA and Al by a spot welding was used. For the evaluation of the adhesion amount of the surface-treated film layer, each test plate of SPC, GA, Al and Mg, and the test plate prepared by joining three metal materials of SPC, GA and Al by spot welding were used. For the evaluation of the coating property, the test plate prepared by joining three metal materials of SPC, GA and Al by spot welding was

used and the test from surface treatment, coating and evaluation of coating property were carried out in series. Fig. 1 is the plane view of the test plate prepared by joining three metal materials of SPC, GA and Al by spot welding and Fig. 2 is an elevation view of it. The numeral 1 indicates a spot welded portion.

- SPC: cold-rolled steel plate (JIS-G-3141)
- GA: both-side alloyed hot-dip zinc-coated steel plate (45 g/m<sup>2</sup>)
- Al: aluminum alloy plate (6000 series aluminum alloy)
- Mg: magnesium alloy plate (JIS-H-4201)

#### Treating process

The treating process of the Examples and Comparative Examples are shown as follows.

Examples 1-4, Example 7 and Comparative Examples 1-4:

alkali degreasing → rinsing by water → film-forming treatment  
→ rinsing by water → rinsing by pure water → drying

Example 5: alkali degreasing → rinsing by water → electrolysis  
formation treatment → rinsing by water → rinsing by Pure water  
→ drying

Example 6: film-formation treatment (used both as degreasing)  
→ rinsing by water → rinsing by pure water → drying

Example 8: alkali degreasing → rinsing by water → film  
formation treatment → rinsing by water → after treatment →  
rinsing by pure water → drying

Example 9: film-formation treatment (and degreasing) → rinsing  
by water → after treatment → rinsing by pure water → drying

Comparative Example 5: alkali degreasing → rinsing by water → surface conditioning → zinc phosphate treatment → rinsing by water → rinsing by pure water → drying

In above mentioned processes for Examples and Comparative Examples, alkali degreasing was carried out as follows. That is, Fine Cleaner L4460 (Trade Mark: Product of Nihon Parkerizing) was diluted to 2% concentration by city water, and was sprayed onto a plate to be treated at 40°C for 120 sec. Rinsing by water and rinsing by pure water after film-formation treatment were performed by spraying water and pure water onto the plate to be treated at a room temperature for 30 sec, both in the Examples and Comparative Examples.

#### Example 1

An aqueous solution of zirconium with a concentration of 200 ppm was prepared using a zirconium oxynitrate reagent and nitric acid. After heating the aqueous solution to 45°C, the pH was adjusted to 3.0 using a sodium hydroxide reagent and hydrofluoric acid and the concentration of free fluorine ion, measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd), was adjusted to 1 ppm, thus obtaining the treating solution for the surface treatment of a metal. The total fluorine concentration in the treating solution for the surface treatment of a metal after adjusting free fluorine ion was 50 ppm.

The test plate rinsed by water after degreasing was immersed into the treating solution for the surface treatment of a metal for 120 seconds so as to carry out the surface treatment.

Example 2 An aqueous solution of zirconium with a concentration of 100 ppm, magnesium with a concentration of 5000 ppm, strontium with a concentration of 2000 ppm and a nitric acid group with a concentration of 28470 ppm was prepared using a zirconium oxynitrate reagent, a magnesium

nitrate reagent and a strontium nitrate reagent. After heating the aqueous solution to 50°C, the pH was adjusted to 4.0 using an ammonium water reagent and hydrofluoric acid, and the concentration of free fluorine ion measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 80 ppm, thus obtaining the treating solution for the surface treatment of a metal. The total fluorine concentration in the treating solution for the surface treatment of a metal, after adjusting free fluorine ion, was 2000 ppm.

The test plate rinsed by water after degreasing was immersed into the treating solution for the surface treatment of a metal for 60 seconds so as to carry out the surface treatment.

### Example 3

An aqueous solution of zirconium with a concentration of 1000 ppm, titanium with a concentration of 2000 ppm, calcium with a concentration of 5 ppm and a nitric acid group with a concentration of 1000 ppm was prepared using an aqueous solution of hexafluorozirconic acid (IV), an aqueous solution of titanium sulfate (IV) and a calcium sulfate reagent. After heating the aqueous solution to 40°C, the pH was adjusted to 5.0 using a potassium hydroxide reagent and hydrofluoric acid and the concentration of free fluorine ion, measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd), was adjusted to 25 ppm, thus obtaining the treating solution for the surface treatment of a metal. The total fluorine concentration in the treating solution for the surface treatment of a metal, after adjusting free fluorine ion, was 2250 ppm.

The test plate rinsed by water after degreasing was immersed into the treating solution for the surface treatment of a metal for 90 seconds so as to carry out the surface treatment.

## Example 4

An aqueous solution of titanium with a concentration of 5000 ppm, strontium with a concentration of 5000 ppm, a nitric acid group with a concentration of 7080 ppm and a nitrous acid group with a concentration of 40 ppm was prepared using an aqueous solution of hexafluorotitanium acid (IV), strontium nitrate reagent and sodium nitrite reagent. After heating the aqueous solution to 35°C the pH was adjusted to 4.0 using a triethanol amine reagent and hydrofluoric acid and the concentration of free fluorine ion, measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd), was adjusted to 10 ppm, thus obtaining the treating solution for the surface treatment of a metal. The total fluorine concentration in the treating solution for the surface treatment of a metal, after adjusting free fluorine ion, was 11900 ppm.

The test plate was rinsed by water after degreasing, then the obtained treating solution for the surface treatment of a metal was sprayed onto the surface thereof for 120 sec., thus carrying out the surface treatment.

## Example 5

An aqueous solution of zirconium with a concentration of 5 ppm, titanium with a concentration of 5 ppm, magnesium with a concentration of 100 ppm, a nitric acid group with a concentration of 30520 ppm and a chloric acid group with a concentration of 100 ppm was prepared using a zirconium oxynitrate reagent, an aqueous solution of hexafluorotitanic acid (IV), a magnesium nitrate reagent, nitric acid and a sodium chloric acid reagent. After heating the aqueous solution to 30°C, the pH was adjusted to 6.0 using an ammonia water reagent and hydrofluoric acid and the concentration of free fluorine ion, measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd), was adjusted to 0.5 ppm, thus obtaining the treating solution for the surface treatment of a metal. The total fluorine concentration in the

treating solution for the surface treatment of a metal, after adjusting free fluorine ion, was 12 ppm.

Using the test plate rinsed by water after degreasing as a cathode and a carbon electrode as an anode, the test plate was electrolyzed in the treating solution for the surface treatment of a metal for 5 seconds under the condition of  $5A/dm^2$ , thus carrying out the surface treatment.

#### Example 6

An aqueous solution of zirconium with a concentration of 150 ppm, magnesium with a concentration of 10 ppm, a nitric acid group with a concentration of 5200 ppm and a hydrogen peroxide concentration of 10 ppm was prepared using a zirconium oxynitrate reagent, a magnesium oxide reagent, nitric acid, and a hydrogen peroxide reagent. After heating the aqueous solution to  $50^{\circ}C$ , the pH was adjusted to 5.0 using an ammonia water reagent and hydrofluoric acid, the concentration of free fluorine ion measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd), was adjusted to 50 ppm and 2 g/L of polyoxyethylenenonylphenylether (ethylene oxide addition mole number: 12 mol), which is a nonionic surface-active agent, was added, thus obtaining the treating solution for the surface treatment of a metal. The total fluorine concentration in the treating solution for the surface treatment of a metal, after adjusting free fluorine ion, was 170 ppm.

On an undegreased test plate on which oil is coated, the above-mentioned treating solution for the surface treatment of a metal was applied to the surface by spraying for 90 sec., thus the degreasing and surface treatment were carried out at the same time.

#### Example 7

An aqueous solution of titanium with a concentration of 100 ppm, calcium with a concentration of 50 ppm, magnesium with a concentration of 5000 ppm, nitric acid group with a



concentration of 25660 ppm and permanganate with a concentration of 10 ppm was prepared using an aqueous solution of titanium sulfate (IV), a calcium nitrate reagent, a magnesium nitrate reagent and a potassium permanganate reagent. A water-soluble acrylic polymer compound (Jurymer AC-10L: product of Nihon Junyaku Co., Ltd.) was added in the aqueous solution so that the concentration of solids was 1%, then the aqueous solution was heated to 50°C. Thereafter, the pH was adjusted to 3.0 using a sodium hydroxide reagent and hydrofluoric acid, and the total free fluorine ion concentration in the aqueous solution to be measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 95 ppm, thus obtaining the treating solution for the surface treatment of a metal. After adjusting the free fluorine ion concentration, the total fluorine concentration in the treating solution for the surface treatment of a metal was 2000 ppm.

The test plate rinsed by water after degreasing was immersed into the treating solution for the surface treatment of a metal for 60 seconds so as to carry out the surface treatment.

#### Example 8

An aqueous solution with 1% of a water-soluble acrylic polymer compound (Jurymer AC-10L: product of Nihon Junyaku Co., Ltd.) in solids concentration and 2g/L of a phosphoric acid reagent as phosphoric acid group was prepared. This aqueous solution was heated to 40°C, then the pH was adjusted to 4.5 using an ammonia water reagent, thus obtaining the after-treating solution. The test plate on which a film formation was carried out by the surface treatment of Example 5 and rinsed by water was dipped into the above-mentioned after-treating solution for 30 seconds so as to carry out the after-treatment.

## Example 9

An aqueous solution of zirconium with a concentration of 50 ppm and cobalt with a concentration of 50 ppm was prepared using an aqueous solution of hexafluorozirconic acid (IV) and cobalt nitrate reagent. After heating the aqueous solution to 40°C, the pH was adjusted to 5.0 with an ammonia water reagent, thus obtaining the after-treating solution. The test plate on which film formation was carried out by the surface treatment of Example 6 and rinsed by water was immersed into the above-mentioned after-treating solution for 30 seconds so as to carry out the after-treatment.

## Comparative Example 1

An aqueous solution of zirconium with a concentration of 500 ppm, magnesium with a concentration of 1000 ppm and a nitric acid group with a concentration of 6780 ppm was prepared using a zirconium oxynitrate reagent, magnesium nitrate and nitric acid. After heating the aqueous solution to 45°C, the pH was adjusted to 4.0 with a sodium hydroxide solution, thus obtaining the treating solution for the surface-treatment of a metal. The free fluorine ion concentration of the treating solution for the surface treatment of a metal was measured by a fluorine ion meter on the market (IM-55G; product of Toa Denpa Industries Co., Ltd), and the result was 0 ppm.

The test plate, which was rinsed by water after degreasing, was immersed into the above-mentioned treating solution for the surface treatment of a metal for 120 seconds so as to carry out the surface treatment.

## Comparative Example 2

An aqueous solution of titanium with a concentration of 2000 ppm was prepared by using an aqueous solution of titanium sulfate (IV). After heating the aqueous solution to 50°C, the pH was adjusted to 3.5 using an ammonia water reagent and hydrofluoric acid, and the concentration of free fluorine ion

measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 400 ppm, thus obtaining the treating solution for the surface treatment of a metal.

The test plate, which was rinsed by water after degreasing, was immersed into the above-mentioned treating solution for the surface treatment of a metal for 90 seconds so as to carry out the surface treatment.

#### Comparative Example 3

Alchrom 713 (Trade Mark, product of Nihon Parkerizing Co., Ltd.), which is the chromic chromate treating agent on the market, was diluted by city water to the concentration of 3.6%, then the total acidity and free acid acidity were adjusted to the center value described in the brochure.

The test plate was rinsed by water after degreasing, then immersed into the chromate treating solution heated to the temperature of 35°C and chromate treatment was carried out for 60 sec.

#### Comparative Example 4

Palcoat 3756 (Trade Mark, product of Nihon Parkerizing Co., Ltd.), which is a chrome-free treating agent on the market, was diluted by city water to the concentration of 2%, then the total acidity and free acid acidity were adjusted to the center value described in the brochure. The test plate was rinsed by water after degreasing, then immersed into the chrome-free treating solution heated to the temperature of 40°C and chrome-free treatment was carried out for 60 sec.

#### Comparative Example 5

The test plate was rinsed by water after degreasing, then the solution prepared by diluting Prepalene ZN (Trade Mark, product of Nihon Parkerizing Co., Ltd.), which is a surface-conditioning agent, with city water to the concentration of 0.1% was sprayed thereon at room temperature for 30 sec. Palbond L3020 (Trade Mark, product of Nihon Parkerizing Co.,

Ltd.) was diluted to the concentration of 4.8% with city water. Further, a sodium hydrogen fluoride reagent as fluorine was added into the solution to 200 ppm and, then, the total acidity and free acid acidity thereof were adjusted to the center value described in the brochure. Thus the zinc phosphate treating solution was prepared. The above-mentioned test plate was immersed into the zinc phosphate chemical treating solution heated to the temperature of 42°C, and a zinc phosphate film was deposited.

#### Evaluation of surface-treated film

The appearance of the surface-treated plates of the Examples and Comparative Examples were evaluated by visual inspection. The results are summarized in Table 1. Further, the adhesion amounts of the surface-treated film layers were measured by a fluorescent X-ray analyzer (System 3270, product of Rigaku Denki Kogyo Co., Ltd.). The results are summarized in Table 2 and Table 3. The adhesion amount of the surface-treated film layer was measured in the case where the metal materials were not joined together and treated respectively (in the case without joining) and in the case where the materials were subjected to joining treatment by means of spot welding (in the case with joining).

Table 1

	appearance after surface treatment		
	on SPC	on GA	on Al
Example 1	uniform interference color	uniform dark black	uniform white
Example 2	uniform interference color	uniform dark black	uniform white
Example 3	uniform interference color	uniform dark black	uniform white
Example 4	uniform interference color	uniform dark black	uniform white
Example 5	uniform interference color	uniform dark black	uniform white
Example 6	uniform interference color	uniform dark black	uniform white
Example 7	uniform interference color	uniform dark black	uniform white
Comparative Example 1	film not deposited	film not deposited	uneven white
Comparative Example 2	pale yellow	uneven gray	uneven white
Comparative Example 3	film not deposited	slightly turned to yellow	gold
Comparative Example 4	film not deposited	film not deposited	uniform white
Comparative Example 5	material partially exposed	uniform gray	uneven white

In Table 1, the appearance evaluation results of the surface-treated films obtained by Examples and Comparative Examples are shown. In the Examples, it is clear that uniform films were obtained on all metal materials in all test plates. Further, on the spot welded portions of the test plates used in the Examples, the deposition of a surface-treated film was observed too. On the other hand, in the Comparative Examples, a uniform film was not formed on all the test plates. Especially, in Comparative Examples 3, 4 and 5, the deposition of a film on spot-welded portions was not at all observed. Further, Comparative Example 5 used the zinc phosphate

chemical-treating solution to be used in the case where a cold-rolled steel plate, zinc-plated steel plate and aluminum alloy are treated at the same time. When the test plates were joined by spot welding as illustrated in the present test, the portion where the metal material was exposed, which is called as "Lack of Hiding", was observed on the cold-rolled steel plate.

Table 2

	adhesion amount of surface treated film layer (without joining) (total adhesion amount of Zr and Ti: mg/m <sup>2</sup> )			
	on SPC	on GA	on Al	on Mg
Example 1	122	67	48	45
Example 2	108	66	49	41
Example 3	61	58	42	38
Example 4	73	59	14	12
Example 5	41	52	38	26
Example 6	35	38	25	19
Example 7	31	29	24	18
Comparative Example 1	trace	trace	trace	trace
Comparative Example 2	25	15	15	10
Comparative Example 3	trace	Cr 33	Cr 95	Cr 75
Comparative Example 4	trace	trace	25	15
Comparative Example 5	weight of film 2.5g/m <sup>2</sup>	weight of film 4.5g/m <sup>2</sup>	weight of film 1.2g/m <sup>2</sup>	weight of film 0.5g/m <sup>2</sup>

Table 3

	Adhesion amount of surface-treated film layer (with joining) (total adhesion amount of Zr and Ti: mg/m <sup>2</sup> )		
	on SPC	on GA	on Al
Example 1	125	67	48
Example 2	118	66	49
Example 3	65	58	42
Example 4	72	59	14
Example 5	45	52	38
Example 6	38	38	25
Example 7	32	29	24
Comparative Example 1	trace	trace	trace
Comparative Example 2	28	17	12
Comparative Example 3	trace	Cr 35	Cr 85
Comparative Example 4	trace	trace	21
Comparative Example 5	weight of film 2.8 g/m <sup>2</sup>	weight of film 4.7 g/m <sup>2</sup>	Weight of film 0.7 g/m <sup>2</sup>

In Table 2 and Table 3, the results by the measurement of the adhesion amount of the surface-treated film obtained in the Examples and Comparative Examples. In the Examples, the aimed adhesion amounts were obtained on all metal materials in all test plates. Further, the adhesion amount of the surface-treated film layer in the Examples was constant, regardless of whether the test plates were joined or not. On the other hand, as clearly understood from the evaluation results for the appearance of a film in the Comparative Example, a uniform film was not deposited on all test plates.

#### Evaluation of coating performance (Preparation of evaluation plate)

For the purpose of evaluating the coating property of the surface treated plates obtained in the Examples and Comparative Examples, coating was carried out by the following process:

cationic electrodeposition coating → rinsing with pure water  
→ baking → surfacer → baking → top coating → baking.

Details of the cationic electrodeposition coating, surfacer, and top coating are as follows:

- Cationic electrodeposition coating: epoxy type cationic electrodeposition coating (Elecron 9400, product of Kansai Paint CO., LTD), electric voltage 200V, thickness of film 20μm, baked at 175°C for 20 minutes,
- surfacer: aminoalkyd coating (AmilacTP-37 gray: product of Kansai Paint CO., LTD.), spray coating, thickness of film 35μm, baked at 140°C for 20 minutes, and
- top coating: aminoalkyd coating (AmilacTM-13 white, product of Kansai Paint CO., LTD.), spray coating, thickness of film 35μm, baked at 140°C for 20 minutes.

#### Evaluation of coating performance

The coating property in the Examples and Comparative Examples was evaluated and the results thereof are shown in Table 4 and Table 5. The items were evaluated and the abbreviations are described below. Hereinafter, the coated film after the electrodeposition coating process is called an electrodeposition-coated film and the coated film after top coating is called a 3-coats film.

- (1) SST: salt water spray test (electrodeposition-coated film)
- (2) SDT: warm salt water dipping test (electrodeposition coated film)
- (3) 1st ADH: primary adhesion (3-coats film)
- (4) 2nd ADH: water-resistant secondary adhesion (3-coats film)

SST: A cross-cut line is notched using a sharp knife on the electrodeposition coated plate and 5% brine is sprayed onto the plate for 840 hours (according to JIS-Z-2371). After spraying, maximum blister widths at both sides from the cross-cut line were measured.



SDT: The electrodeposition-coated plate was soaked in aqueous solution of 5 wt% of NaCl at 50°C for 840 hours. After soaking, the test plate was washed with city water and dried at room temperature. The whole surface of the test plate peeled off using an adhesive tape and the removed area of the coated film on each metal material was evaluated by an inspector's eye.

1<sup>st</sup> ADH: Checker lines of 100 squares with 2 mm intervals were marked using a sharpened knife on a 3-coats film. The squares in the checker were peeled using a cellophane tape and the numbers of peeled squares were counted.

2<sup>nd</sup> ADH: A 3-coats film was soaked in pure water at 40°C for 240 hours. Then, 100 checker squares with 2mm interval were marked using a sharpened knife on it. The checker squares were peeled using a cellophane tape and the numbers of peeled squares were counted.

Table 4

	coating property of electrodeposition film					
	SST max blister widths at both sides (mm)			SDT Removed area (%)		
	on SPC	on GA	on Al	on SPC	on GA	On Al
Example 1	2.0	0.5	0.5	5>	5>	5>
Example 2	2.0	0.5	0.5	5>	5>	5>
Example 3	3.0	0.5	0.5	5>	5>	5>
Example 4	3.0	0.5	0.5	5>	5>	5>
Example 5	3.0	0.5	0.5	5	5>	5>
Example 6	3.5	1.0	0.5	10	5>	5>
Example 7	3.5	1.0	0.5	10	5>	5>
Example 8	2.5	0.5	0.5	5>	5>	5>
Example 9	2.5	0.5	0.5	5>	5>	5>
Comparative Example 1	6.5	3.5	3.0	70	40	15
Comparative Example 2	4.5	2.0	0.5	30	10	5
Comparative Example 3	10.0	5.0	0.5	80	40	5>
Comparative Example. 4	10.0	5.0	1.0	90	50	10
Comparative Example 5	5.0	2.0	2.0	40	10	20

The results for the evaluation of the coating property of the electrodeposition-coated film are summarized in Table 4. The Examples showed a good corrosive resistance on all test plates. On the other hand, in Comparative Example 1, since free fluorine ions were not contained in the treating solution for the surface treatment of a metal, the deposition of the surface-treated film was not sufficient and thus the corrosion resistance was not so good. Further, in Comparative Example 2, since the concentration of free fluorine ion in the treating solution for the surface treatment of a metal was high, especially, the adhesion amount of a film on SPC was small and the corrosion resistance was not so good. The coating properties of Examples 5 and 6 were superior to those of Comparative Examples, but when compared with other Examples, corrosive resistances after electrodeposition coating was inferior to those of other Examples. However, as shown in Examples 8 and 9, the corrosive resistance was further improved by carrying out the after-treatment.

Because in Comparative Example 3, a chromate treating agent for an aluminum alloy was used and in Comparative Example 4, a chrome free-treating agent for an aluminum alloy was used, the corrosion resistance of the Al was good but the corrosion resistance of other test plates were obviously inferior to those of the Examples. In Comparative Example 5, a zinc phosphate treating agent, which is now usually used as the base for coating was used. However, Comparative Example 5, in the condition where each of the test plates was joined by welding, showed test results inferior to those of Examples.

Table 5

	coating properties of 3-coats film					
	1st ADH			2nd ADH		
	on SPC	on GA	on Al	on SPC	on GA	on Al
Example 1	0	0	0	0	0	0
Example 2	0	0	0	0	0	0
Example 3	0	0	0	0	0	0
Example 4	0	0	0	0	0	0
Example 5	0	0	0	0	0	0
Example 6	0	0	0	0	0	0
Example 7	0	0	0	0	0	0
Example 8	0	0	0	0	0	0
Example 9	0	0	0	0	0	0
Comparative Example 1	0	0	0	5	8	0
Comparative Example 2	0	0	0	0	0	0
Comparative Example 3	6	0	0	17	3	0
Comparative Example 4	0	0	0	5	0	0
Comparative Example 5	5	0	0	8	0	6

Table 5 shows the evaluation results of the adhesion of a 3-coats plate. The Examples showed a good adhesion to all test plates. Regarding the 1st ADH, good results were obtained in all the Comparative Examples. However, regarding the 2nd ADH, the Comparative Examples did not show a good level of adhesion to all the test plates the same as the corrosive resistance of the electrodeposition coating. Further, in Comparative Example 5, the generation of a sludge, which is the by-product of zinc phosphate treatment, was observed in the treating bath after the surface treatment. However, in the Examples of the present invention, the generation of a sludge was not observed.

From the above-mentioned results, it is obviously understood the following facts. That is, simultaneous treatments of SPC, GA, and Al and the deposition of a surface-treated film having a good adhesion and corrosion resistance on the surface thereof without changing the treating bath and treating conditions are possible only by using the treating solution for the surface treatment of a metal and the surface-

treating method of the present invention. According to the present invention, it is possible to deposit a surface-treated film having a good corrosion resistance, even on a welded portion. Further, since the method for the surface treatment of the present invention requires only to bring the metal material to be treated in contact with the treating solution for the surface treatment of a metal, it is possible to deposit a surface-treated film and improve the corrosive resistance in the portion where the solution may not be stirred, such as the inside of bag-shaped structure.

#### Industrial Applicability

According to the treating solution for metal surface treatment and the method for surface treatment of the present invention, it is possible to deposit a surface-treated film having an excellent corrosion resistance after coating on the surface of a metal made of two or more, or each of a ferriferous material, a zinciferous material, an aluminiferous material and a magnesiferous material in the treating bath containing no harmful component to the environment and without generating a sludge, which have never been achieved in the prior art. Further, since the present invention does not need a process for surface conditioning on the metal material to be treated, it is possible to shorten the treatment time and to reduce the space for the treatment.